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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.473065

On the magnetic coupling in NiO

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(Received 14 August 1996; accepted 29 October 1996)

The results are reported of *ab initio* calculations on the magnetic ordering in NiO, a prototype of the antiferromagnetic insulator. By analyzing wave functions for different cluster models, information is obtained about the physical effects determining the sign and the magnitude of the magnetic coupling parameter J. The role of the edge oxygens, surrounding the essential unit (Ni_2O), is found to be quantitatively important but purely environmental in contrast to the role of the bridging oxygen. Furthermore, the importance of electron correlation and the usefulness of pseudopotentials in the calculations is investigated. The final result for J compares reasonably with experiment (about 50%), and possible sources for the remaining discrepancies are discussed. © *1997 American Institute of Physics.* [S0021-9606(97)02805-5]

I. INTRODUCTION

The magnetic properties of the first-row transition metal compounds remain a challenging and interesting problem for theoretical work. The transition metal oxides gained special interest because of their close relation to the parent compounds of the high-T_c superconductors. The most common magnetic ordering observed in transition metal oxides is antiferromagnetism. *Ab initio* quantum chemistry not only offers the tools to compute the magnitude of the antiferromagnetic coupling, but also the means to extract information about the mechanisms determining this magnitude.

The fundament for quantum chemical calculations on the magnetic coupling lies in the Heisenberg Hamiltonian,[1] a two body interaction operator. From there it is easily derived that J might be obtained from the energy difference of the spin states, arising from the possible couplings of the spin moments on the two magnetic centres. These energies can be calculated with several quantum chemical techniques, systematically improving the description of the electronic structure and thus obtaining information about the physical effects determining the magnitude of J.

The first application of *ab initio* quantum chemical techniques to magnetic ordering in transition metal compounds was made by Wachters and Nieuwpoort, who calculated J in $KNiF_3$.[2] Recently work has been done in this field by Casanovas *et al.* on $KNiF_3$,[3,4] and La_2CuO_4[5] and by van Oosten *et al.* on several cuprate compounds.[6,7] Their investigation of the J parameter led to rather close agreement with experimental values and to more detailed insight into the mechanism that determine J. Casanovas *et al.* found the magnitude of J to be built up by three distinguishable mechanisms: the mixing of the metal d-(magnetic) orbitals with the anion p-orbitals, electron correlation effects, and collective effects. Van Oosten *et al.* found that including configurations connected to charge transfer excitations from the bridging ligand strongly enhances the calculated J, provided that orbital relaxation for these configurations is accounted for in the wave function.

In this paper we present the results of *ab initio* calculations on the magnitude of J in NiO, a prototype of the type II antiferromagnetic ordering. The magnetic ordering in these materials is determined by the next-nearest neighbor ions in the [100] direction, and is parametrized by J. The nearest neighbor interactions in the [110] direction cancel out in an ideal structure, six parallel and six anti-parallel spins for each nickel ion.

Experimentally J is obtained with different techniques. In 1972 Hutchings and Samuelsen determined J by neutron scattering[8] to be -19.0 meV. Because of small lattice distortions they also found a net value for the nearest neighbor interaction. This interaction was given as 1.4 meV, indeed very small, but ferromagnetic. Interpretation of other experimental data by Shanker and Singh[9] led to a J-value of -17.3 meV and to a small antiferromagnetic nearest neighbor interaction. More recent (1990) are the Raman scattering measurements of Massey and co-workers. They estimated the pressure dependence of J.[10] At the lattice parameter we used in the calculations (2*3.9344 bohr) J has the value of -19.8 meV.

The magnetic properties of NiO were the subject of previous semi-empirical investigations. Setting up model Hamiltonians and using different parametrization schemes, the experimental value of J could be reproduced with reasonable accuracy.[11,12] Band structure calculations using the local density approximation led to an overestimation of J by a factor of 3.[13,14] The J value in the present *ab initio* approach agrees fairly well with the experimental value. Moreover, this approach enables one to evaluate the importance of different physical mechanisms that contribute to the magnetic coupling.

II. COMPUTATIONAL INFORMATION

A. Material model

Two different material models are used to study the physical effects determining J. The first one contains only

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the most essential part needed to describe the process of superexchange, i.e., two Ni^{2+} ions and a bridging oxygen (Ni–O–Ni; Ni_2O). The nickel ions each have a net spin moment of 1, that couple to singlet, triplet, and quintet states. The second cluster model extends the first model by including all oxygen ions directly surrounding the two Ni ions (Ni_2O_{11}).

In both cases the rest of the crystal is represented by point charges, that reproduce the external Madelung potential in the cluster region.[15] The nickel oxygen distance (3.9344 bohr) was taken from experiment.[16] In both models the bridging oxygen is surrounded by four pseudopotentials as an improvement of the point charge approximation. These pseudopotentials represent the Ni^{2+} ions by a nickel core potential, with an effective nuclear charge of $+2$.

B. Pseudopotentials

To make large calculations feasible it can be necessary to use pseudopotentials instead of including the core electrons explicitly. Such pseudopotentials have shown to be of value in several applications and may well be essential in calculations on magnetic properties of $4d$- and $5d$-transition metal compounds and in calculations on systems with more than two transition metal ions.[3,4] One has to establish, however, whether these potentials can be used for the study of the small energy differences that determine the strength of magnetic couplings. To investigate the usefulness of pseudopotentials in the case at hand, two sets of calculations were performed, with and without pseudopotentials representing the ion cores. For oxygen the $1s$ electrons and for nickel the argon core (up to $3p$) are represented by pseudopotentials.[17,18] The use of pseudopotentials reduces the number of electrons treated explicitly from 162 to 104 in the case of Ni_2O_{11}.

C. Basis sets

In all calculations Gaussian type basis sets with a segmented contraction were used.[3,5,32–34] In Table I an overview is given of all the basis sets used in the different calculations.

In order to compare the calculations with and without pseudopotentials, it is important that the basis sets are of comparable accuracy in both cases. It is impossible to use basis sets of exactly the same quality because a different number of electrons is to be described. We think that the basis sets explored are adequate for the comparison we want to make.

D. Computational methods

The so-called Anderson model[19] is commonly held to contain the essential ingredients that are necessary to obtain superexchange. In the complete active space CI (CASCI) approach, this model is reproduced by carrying out a complete CI in an active space formed by the open shell orbitals centered mainly on the Ni^{2+} ions [$3d(z^2)$ and $3d(x^2-y^2)$]. The orbitals of the high spin state ($^5A_{1g}$), obtained by doing a restricted open shell Hartree–Fock (ROHF) calculation, were used as reference orbitals for the CASCI. This choice is expected to underestimate the antiferromagnetism. The orbitals are fully relaxed for the ferromagnetic state only, causing a relative higher energy for the other spin states.

TABLE I. Overview of basis sets used in the different calculations.

All electron	Ni_2O	Ni_2O_{11}	Ref.
Ni	$(14s,11p,6d)/[6s,5p,4d]$	$(14s,11p,6d)/[6s,5p,3d]$[a]	32
Bridging O	$(9s,5p)/[4s,3p]$[b]	$(9s,5p)/[4s,3p]$[b]	33
Edge O	⋯	$(9s,5p)/[3s,2p]$[c]	33
pseudopotentials			
	Ni_2O	Ni_2O_{11}	Ref.
Ni	$(3s,3p,6d)/[2s,2p,3d]$[d]	$(3s,3p,6d)/[2s,2p,3d]$	3
Bridging O	$(6s,6p)/[3s,3p]$[b]	$(6s,6p)/[3s,3p]$[b]	5
Edge O	⋯	$(6s,6p)/[2s,2p]$	5

[a]The contraction scheme was found by performing a calculation on the Ni^{2+} ions in the field of the other ions using the uncontracted primitive set. (available on request).
[b]A d-function was added ($\zeta=1.25$) (Ref. 34).
[c]The contraction scheme was found by performing a calculation with one oxygen ion in the field of the other ions using the uncontracted primitive set. (available on request).
[d]To study the effect of a more flexible basis set in the d-functions, calculations were also done on the Ni_2O cluster with one more d-function left uncontracted.

To improve on the Anderson model, one has to account for terms not included in this model. These terms, although called differently by different authors, can be attributed to external correlation, i.e., the effect of configurations connected to excitations outside the active space. In the present study various methods were used to include external correlation; first by the perturbational treatment of remaining electron correlation. With multi-configurational second order perturbation theory as described in Refs. 20–22, the effect of single and double excitations with respect to the reference space (in all calculations the CASCI space formed by the open shell orbitals on the Ni^{2+} ions) was taken into account.

These single and double excitations can be classified according to the degrees of freedom they possess. Labeling the orbitals by $i,j,...$ for the inactive, $t,u,...$ for the active, and $a,b,...$ for the virtual orbitals, three different groups of excitation operators can be identified:

with two degrees of freedom: $\hat{E}_{ti}\hat{E}_{uj}$, $\hat{E}_{ti}\hat{E}_{au}$, and $\hat{E}_{at}\hat{E}_{bu}$
with three degrees of freedom: $\hat{E}_{ti}\hat{E}_{aj}$ and $E_{ai}\hat{E}_{bt}$
with four degrees of freedom: $\hat{E}_{ai}\hat{E}_{bj}$.

In the case of a degenerate reference space only the determinants with two degrees of freedom contribute to the energy difference of the states involved.[23,24] To find out if any deviations for a not strictly degenerate reference space (the CASCI reference space) can be observed, the effect of determinants with two degrees of freedom (MP2-2), three degrees of freedom (MP2-3), and four degrees of freedom (full MP2) was investigated within the perturbational approach.

The second method used to improve on the Anderson model is difference dedicated CI (DDCI).[24] The list of exci-

TABLE II. J values for Ni_2O in meV, using pseudopotentials to replace the core electrons compared to all electron calculations. J values are given at the different levels of approximation as described in the text.

	CASCI	MP2-2	MP2-3	MP2	DDCI-2
Pseudopotentials					
E_s-E_t	−1.0	−2.2	−2.1	−2.2	−2.0
$(E_s-E_q)/3$	−0.9	−2.2	−2.1	−2.2	−2.1
All electron					
E_s-E_t	−1.5	−3.5	−3.2	−3.3	−3.5
$(E_s-E_q)/3$	−1.5	−3.3	−3.3	−3.3	−3.5

tations with two degrees of freedom is treated by CI. These calculations are referred to as DDCI-2.

To get more insight into the mechanisms that determine the value of J, two constrained space orbital variations (CSOV) analyses[4,25,26] were made. By starting with two purely ionic fragments, the wave function is fully relaxed in a series of constrained variations in which the variational space is modified in each successive step. At each step J was calculated at the CASCI level only. This is because the methods used to improve on the Anderson model account at each step of the CSOV for at least part of the orbital relaxation, in this way circumventing the constraints given by the CSOV. The first CSOV started with the fragments Ni_2^{4+} and O^{2-} and the second with Ni_2O^{2+} and O_{10}^{20-}, obtained from ROHF calculations. In these calculations the all electron approach was used.

All calculations were performed with the PSHF-CIPSI chain of programs, developed at the University of Toulouse, France, the University Rovira i Virgili, Tarragona, Spain, and the University of Barcelona, Spain.[27]

III. RESULTS

A. Ni_2O

The first calculations were done on the Ni_2O cluster using pseudopotentials. In Table II the results of the CASCI, MP2-2, MP2-3, MP2, and DDCI-2 are listed. J is obtained from the energy differences of the singlet, triplet, and quintet energies. At the CASCI level, equivalent to the Anderson model, J is obtained with the correct, antiferromagnetic, sign. Its magnitude is far too small however, as was found before by other authors.[2–7,28–30] Roughly, a doubling of J is obtained by taking the external electron correlation into account. Second order perturbation theory and DDCI-2 both yield essentially the same result. This illustrates that, indeed by second order perturbation theory, only the determinants with two degrees of freedom contribute significantly to the energy differences.

For comparison the same calculations were repeated with a Ni basis set in which one more d-function was left uncontracted. These calculations gave the same J values.

As a next step the all electron calculations on the Ni_2O cluster were done. In Table II the results are collected. To make a fair comparison of all electron versus pseudopotential calculations and to see the influence of core-valence correlation we performed three extra MP2 calculations. Starting with correlating only the Ni-3d electrons, we subsequently allowed first for excitations from the O-2s and 2p orbitals and finally for excitations from the Ni-3s and 3p orbitals as well. In Table III the results of these MP2 calculations are listed.

TABLE III. J values for Ni_2O in meV, all electron. Correlating different number of electrons at the MP2 level of approximation.

	Correlated electrons		
	Ni-3d	...+O-2s,2p	...+Ni-3s,3p
E_s-E_t	−2.9	−3.1	−3.3
$(E_s-E_q)/3$	−2.9	−3.1	−3.3

The all electron calculations confirm the observations made in the calculations with the pseudopotentials. At the CASCI level the correct magnetic ordering is obtained, external electron correlation drastically increases J, and essentially the same value is obtained at all MP2 approximations. Treating the determinants with two degrees of freedom in a CI (DDCI-2) gives a slightly higher J value.

A comparison of the pseudopotentials versus all electron results can be made at two points, i.e., CASCI and MP2 with the same set of electrons correlated (the second column in Table III). The pseudopotentials influence the value of J, they decrease J by 39% for CASCI (−1.5 versus −1.0) and by 28% for MP2 (−3.1 versus −2.2). From Table III the conclusion can be extracted that correlating the Ni-3d electrons only gives the essential part of the increase compared to CASCI. Correlating the O-2s, 2p gives a small extra contribution of about 0.2 meV and on top of that the Ni-3s, 3p electrons contribute another 0.2 meV (resulting in the full MP2 value from Table II).

B. Ni_2O_{11}

Previous theoretical work, for example on $KNiF_3$,[4,31] showed that a full coordination of the two magnetic centers, the two Ni^{2+} ions, is important and a rather large increase of the magnetic coupling was observed going from Ni_2F to Ni_2F_{11}. In our second series of calculations we concentrated on the Ni_2O_{11} cluster. Again, the comparison is made between all electron versus pseudopotential calculations and J is estimated at different levels of approximation.

For the Ni_2O cluster model the full MP2 results are essentially the same as those with the DDCI method. Therefore, only CASCI and MP2 calculations were performed for the Ni_2O_{11} cluster model. In Table IV all electron and pseudopotential results are compared. In Table V the results

TABLE IV. J values for Ni_2O_{11} in meV, pseudopotentials versus all electron. J values are obtained at CASCI and MP2 levels.

	Pseudopotentials		All electron	
	CASCI	MP2	CASCI	MP2
E_s-E_t	−3.0	−7.8	−3.8	−10.4
$(E_s-E_q)/3$	−3.0	−7.8	−3.8	−10.6

TABLE V. J values for Ni_2O_{11} in meV, all electron. Correlating different number of electrons at the MP2 level of approximation.

	Ni-3d	...+O-2s,2p	...+Ni-3s,3p
E_s-E_t	−6.2	−10.0	−10.4
$(E_s-E_q)/3$	−6.2	−10.1	−10.6

are listed for the MP2 calculations on the all electron cluster, correlating different electrons (as in Table III).

The influence of the ten edge oxygens is clear. Comparing the Ni_2O and the Ni_2O_{11} results shows that J increases in all cases by approximately a factor of 3. In the next section a more detailed analysis is made of the role of the ten edge oxygens.

Just as in the Ni_2O cluster study it is found that the use of pseudopotentials decreases J. A decrease of more than 20% is observed of the CASCI value (Table IV; column 1 and 3), as well as of the MP2 value (Table IV; column 2 and 4). The comparison is not biased by the difference in basis set quality in the d-functions (see Table I), remembering that the results from the Ni_2O cluster model using pseudopotentials with three and four contracted d-functions were equivalent. We conclude that to describe the magnetic coupling in ionic crystals one has to be very careful using pseudopotentials to describe the core electrons. The potentials influence the value of J.

Table V shows the influence of correlating different sets of electrons. Some closed shell orbitals could not be uniquely attributed to Ni-3d or O-2p electrons, therefore there is some arbitrariness in the headings of the table. In contrast to the Ni_2O case now the O-2s, 2p electrons give a substantial contribution to J of almost 4 meV. This can be explained partly by the larger number of electrons that are correlated, all O-2s, 2p electrons being considered in the calculation, and partly by the mixing of closed shell Ni-3d and O-2p orbitals. Again, there is some contribution of the Ni-3s, 3p electrons; an increase of J by about 0.5 meV is obtained.

C. CSOV analysis

The results from the Ni_2O_{11} cluster model study showed that edge oxygens instead of point charges substantially increase the value of J, and hence play an important role in the description of the magnetic coupling in NiO, although in the models used in the present work they do not participate directly in the superexchange mechanism. In order to get more insight in the role of the edge oxygens, two CSOV analyses were made, one of the Ni_2O cluster model and one of the Ni_2O_{11} cluster model. As described in the computational information the ionic starting points were Ni_2^{4+}, O^{2-}, and Ni_2O^{2+}, O_{10}^{20-} for the two analyses respectively. This choice is slightly different from that in previous work[4,5] but leads to a clearer indication of the role of the ten edge oxygens. In Table VI a detailed overview of the CSOV analyses is given.

TABLE VI. J values for Ni_2O and Ni_2O_{11} in meV, all electrons. J is obtained at the different steps of the CSOV analysis at the CASCI level.

Step in CSOV[a]	Variational space	Ni_2O	Ni_2O_{11}
1. Frozen ions	⋯	−0.2	−3.5
2. Polarization fragment A	doubly occ. A+ virt. A	−0.0	−4.5
3. Charge transfer A→B	doubly occ. A+ virt. A+virt. B	−0.1	−4.1
4. Polarization of B[b]	doubly occ. B+ virt. B	−0.1	−4.0
5. Charge transfer B→A	doubly occ. B+ virt. A+virt. B	−0.1	−3.9
6. Mixing open and closed shells	doubly occ. A & B +open A	−1.5	−3.7
SCF	full space	−1.5	−3.8

[a]Fragment A refers to Ni_2^{4+} and Ni_2O^{2+}, respectively, fragment B refers to O^{2-} and O_{10}^{20-}, respectively.
[b]In the successive steps the orbitals that are kept frozen are always obtained from the previous step.

In the table only one J value is listed, the difference of singlet and triplet energy, because the other is essentially the same.

The first column in Table VI clearly illustrates the superexchange mechanism. J is completely determined by the mixing of the open shell orbitals on the nickels and the O-2p orbital, i.e., by introducing covalency in the Ni_2O cluster model. From the second column it is obvious that the role of the edge oxygens is different from that of the bridging ligand. On superimposing the two ionic fragments, Ni_2O^{2+} and O_{10}^{20-}, not allowing for any covalent interaction between the two, the J of the fully relaxed cluster model is already recovered almost completely.

IV. DISCUSSION AND CONCLUSIONS

CASCI calculations, which are equivalent to the Anderson model, give J values that have the correct antiferromagnetic sign, but which are far too small. The Anderson model is improved by including external correlation, via second order perturbation theory or difference dedicated CI.

The reference space used in the calculations to improve on the Anderson model is not exactly degenerate. Therefore, strictly speaking, the observation of Malrieu *et al.*[23,24] that only determinants with two degrees of freedom contribute to the energy differences of the spin states is not applicable to this case. Nevertheless, the results on the Ni_2O cluster model (Table II) show that the deviations from the ideal case, with a strictly degenerate reference space are rather small. Hence, the application of the DDCI-2 (a CI taking the determinants with two degrees of freedom only) is justified.

The different cluster model studies combined with the CSOV analysis clearly indicate some physical mechanisms that contribute to the magnitude of the antiferromagnetic coupling. First, we recognize the well known superexchange mechanism in the Ni_2O cluster model by the observation that J is essentially determined by the covalency introduced when the open shell orbitals on nickel are allowed to mix with the O-2p orbitals. Second, the role of the edge oxygens

is elucidated from the Ni_2O_{11} cluster model calculation. Covalency is not involved in the mechanism that increases J when the edge oxygens are added. The role of the edge oxygens in these cluster model descriptions is purely environmental. In the real material, however, these oxygens play the role of bridging oxygen as well. Another important mechanism recognized is the external electron correlation, it increases J by roughly a factor of 3.

Comparison of all electron results with results obtained with pseudopotentials representing the Ni-1s,….3p electrons and O-1s electrons shows that the potentials do influence the calculated value of J: they decrease J by 20–40%.

About 50% of the experimental value is obtained with the present *ab initio* cluster model study. There are several reasons that explain this discrepancy; for example, the embedding of the ten edge oxygens. For the same reason that embedding the bridging oxygen in a shell of pseudopotentials increases J, a similar effect might appear by adding a shell of pseudopotentials around the edge oxygens. A contribution from collective effects is not to be excluded and is still under investigation. The effect of increasing the basis set is expected to be small as previous work showed.[4] A more drastic increase of J should be found introducing the O-2p_σ into the CASCI space, leading to a more complete description of the charge transfer excitations from the central oxygen. These contributions were found to be very important by van Oosten *et al.*[6,7] In the present description part of this effect is included in the MP2 step following the CASCI, but essential details as proper orbital relaxation and the coupling matrix elements between the charge transfer excitations and external excitations are not included.

ACKNOWLEDGMENTS

We thank Professor R. Caballol for pertinent remarks. This research is partially supported by the Human Capital and Mobility Programme, Access to Large Installations, under Contract No. CHGE-CT92-0009, ''Access to supercomputing facilities for European researchers,'' established between the European Community and CESCA/CEPBA.

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